

A PHYSICO-CHEMICAL INVESTIGATION OF EASTERN AND WESTERN SHALE OILS PRODUCED BY THE IGT HYTORT AND FISCHER ASSAY PROCESSES

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INTRODUCTION

The major interest in oil shale development within the United States, thus far, has focused on the oil shales in the Green River Formation in Colorado, Utah and Wyoming. However, a substantial portion (nearly 250,000 square miles) of the Eastern United States is underlain by the Devonian Black Shales, and in principle, represents a sizeable potential resource. These shales, however, yield only less than one-half as much liquids upon heating as do the Green River Formation oil shales, because of the lesser hydrogen contents of the Devonian shales. Therefore, processes to extract liquids or improve recovery ratios from the Devonian shales must necessarily deal with special retorting techniques for hydrogen deficient materials. One such candidate process is the Institute of Gas Technology's Hytort process, which retorts oil shale under hydrogen pressure with the result that oil yields of Devonian shales are increased 2.5 times over those obtained by the standard Fischer assay. Characterization of the Eastern and Western oils that are produced by the IGT and Fischer assay processes would be beneficial toward: a) assessing the quality of the product oils, b) understanding the retort process and c) providing information for optimizing the process.

Nuclear Magnetic Resonance (NMR) is a technique that has been used extensively to characterize petroleum fractions. An advantage of NMR is that it can be applied to whole oils to determine gross compositional and structural changes that might occur during the process. This information in turn, can be used by process engineers to determine what parameters to vary or control, and by chemists to determine the need for further fractionation and characterization.

This paper reports the results of NMR studies of shale oils produced by the IGT Hytort and Fischer assay processes and hydrotreated shale oils from the Hytort process. The Fischer assay is the standard method for evaluating an oil shale's potential for conversion to liquids and thus, oils produced from the Fischer assay represent baseline oils for comparison purposes. Few papers have appeared on the analysis of shale oils using NMR techniques(1,2). Those that have, have discussed shale oils produced primarily from Green River oil shales. Shale oils produced from Eastern oil shales, coupled with the ones produced from processes other than the Fischer assay, offer a set of shale oils different enough to assess the utility of NMR methods.

EXPERIMENTAL PROCEDURE

A. Shale Oil Source

The NMR studies were conducted on shale oils obtained from a Western Eocene shale (Colorado, Piceance Basin) and two Eastern Devonian shales (Kentucky Sunbury and Kentucky New Albany from Lewis and Bullitt Counties, Kentucky, respectively). The shale oils from the three shales were obtained using the IGT Hytort Process Development Unit at IGT(3) and the Fischer Assay retort method at LETC(4). The Eastern shale oils were further upgraded using the IGT catalytic hydrotreating unit at IGT(5).

B. Nuclear Magnetic Resonance

Samples were prepared in 5mm tubes for ^1H and 10mm tubes for ^{13}C experiments. Tetramethylsilane (TMS) was used as a reference for both nuclei and CDCl_3 as the solvent for all samples. Concentrations of approximately 50/50 and 65/35 by volume of sample to solvent were used for proton and carbon-13 spectra, respectively. Six percent TMS in CDCl_3 provided the lock signal for ^1H and the solvent CDCl_3 provided the lock signal for ^{13}C NMR spectra.

C. Average Molecular Structure Parameters

The average molecular structure parameters for the various shale oils were calculated from the normalized ^1H and ^{13}C spectral areas. The equations used to compute the parameters were assembled from the literature and partly derived by Netzel and Hunter(6). The equations were modified to include the presence of olefins(7).

RESULTS AND DISCUSSION

A. Shale Oil - Analytical Data

Table I lists the elemental composition and the H/C weight ratios of the Eastern and Western shale oils obtained from the Fischer assay and IGT Hytort retorting processes. Also included in the Table are the elemental compositions and H/C weight ratio of the hydrotreated shale oils.

As shown in Table I, the H/C weight ratio of the shale oil appears to be independent of the retorting process for a given shale. However, for the hydrotreated IGT Hytort shale oils, the H/C ratio increases as one would expect upon hydrogenation of aromatic and olefinic molecules to form saturate molecules. The H/C weight ratio of the Eastern shale oils are significantly lower than that of the Western shale oil indicating greater aromatic content for the Eastern shale oils.

The total sulfur content of the Western shale oils is lower than the Eastern shale oils and appears to be independent of the retorting process. The nitrogen content is slightly higher for the Colorado shale oil relative to the two Kentucky shale oils. The IGT Hytort process relative to the Fischer assay method tends to increase the nitrogen content of the shale oils independent of the source of the oil shale. This increase may be due to the more severe conditions used in the Hytort process. As expected the hydrotreated shale oils have markedly reduced nitrogen and sulfur contents.

B. Shale Oil - NMR Data

Figure 1 shows the ^1H NMR spectrum of the Colorado Fischer assay shale oil. Most of the quantitative information on the composition of shale oil is derived from the ^1H spectrum since the chemical shift ranges for the various hydrogen types found in hydrocarbons are fairly well defined⁶.

Figure 2 shows the ^{13}C NMR spectra of the Colorado shale oil produced from the Fischer assay method and the IGT Hytort process. The region from 100 to 150 ppm represents the aromatic/olefinic carbon resonances. The two sharp resonances at 114 and 138 ppm are due to 1-alkenes(1). The aliphatic carbon resonances are found in the region from 0 to 50 ppm. The five intense signals (14, 23, 29, 30 and 32 ppm) in this region correspond to the five signals associated with carbon chain greater than 9. The greater the intensity of the resonance at 30 ppm relative to the intensity of the resonance at 14 ppm, the longer the carbon chain length. The less intense signals in this region are due to branched and cyclic alkanes and alkyl groups of alkylaromatics(2). It is not possible to infer the individual molecular species from neither the ^1H nor ^{13}C NMR spectra but only the average molecular type.

Figure 3 shows the carbon-13 spectra of the Kentucky Sunbury shale oils produced by the Fischer assay and the IGT Hytort processes. The two Eastern shale oils produced by the IGT Hytort process were catalytically hydrotreated. The carbon-13 spectrum of the hydrotreated Kentucky New Albany shale oil is shown in Fig. 4. The spectrum of the hydrotreated Kentucky Sunbury is nearly identical and is not given.

C. Average Molecular Structure Parameters

Average molecular structure parameters and the composition of the hydrocarbon types can be determined from the integration of the area of the various carbon and hydrogen regions in the NMR spectra(6). When calculating the average molecular structure parameters for any hydrocarbon mixture including shale oil several assumptions must be made. These assumptions are: (1) The sample contains only mono- and diaromatics which in most cases is valid because the concentration level of triaromatics in shale oil is small, (2) the unsubstituted non-bridged aromatic ring carbon protons of mono- and diaromatics are sufficiently separated in the ^1H spectrum such that the ratio of mono- to diaromatics protons can be determined, (3) the number of substituents in the mono- and diaromatic components is the same, (4) the concentration of heteronuclear molecules is low (a weak assumption), (5) one hydrogen per olefinic carbon and (6) long carbon chain alkyl substituents on aromatic rings and long alkyl carbon chains of olefins are computed as saturate hydrocarbons.

Because the shale oils were collected over a large temperature range, the validity of average structural parameters in representing molecular type is almost meaningless. The structural parameter data are valuable in that they quantitatively represent observed changes in the ^1H and ^{13}C NMR spectra of the shale oils, and thus trends may be established.

Tables II, III, and IV give the average molecular structure parameters. Two important parameters are the hydrogen and carbon aromaticities. The hydrogen aromaticity, f^{H} , is defined as the area measurement of the aromatic hydrogens divided by the total area of all hydrogens in the ^1H spectrum. Values for f^{H} for the Eastern and Western shale oils produced by the Fischer assay, IGT Hytort and the hydrotreated Hytort methods are given in the tables.

The ratio of the integrated aromatic carbon region to the total integrated carbons in the ^{13}C spectrum gives the carbon aromaticity, f^{C} . Carbon aromaticities for the various shale oils are also given in Tables II, III, and IV. It should be noted that the carbon aromaticity value is not totally due to aromatic carbons but also olefinic carbons.

The measurement of f^{H} and f^{C} are obtained directly from their respective NMR spectrum. That is, no assumptions (aside from olefinic contribution to f^{C}) are made in computing these values. Thus these values are important in representing any changes which might occur in a system under retorting conditions or hydrotreating.

Tables II through IV also list the mole percent of hydrocarbon types in the various shale oils. To a very good first approximation, the data can be used to compare shale oil source and retorting methods. To convert the mole percentages to weight or volume percentages requires additional assumptions regarding average molecular weights and average densities for the hydrocarbon types and thus is not germane to the discussion. More so than the H/C weight ratios (Table I), the mole percent of aromatics (which includes nitrogen sulfur and oxygen heteroaromatics), olefins and alkanes in Tables II through IV show clearly the differences in Eastern and Western shale oils obtained from the two retorting and hydrotreating processes.

It is readily seen from the data in Tables II-IV that the Eastern shale oils produced by the Fischer assay method and the IGT Hytort processes contain about twice as much aromatics compared to the Colorado shale oil. For the Colorado shale

oil, the mole percent of aromatics are nearly same regardless of the retort method (probably due to less severe conditions used in the Hytort process). However, for the Eastern shale oils, the IGT Hytort process increases the mole percent of aromatics relative to the Fischer assay method. This increase in aromatics for the Eastern shale oils over the Colorado shale oil is the result of (1) higher aromatics in the raw oil shales which is supported by solid state NMR data and (2) retorting in a hydrogen atmosphere which may free more aromatics from the matrix.

The Fischer assay method produces more olefins for the Colorado shale oil relative to the two Kentucky shale oils (see Tables II-IV), while the IGT Hytort process produces less olefins overall. However, the Colorado Hytort shale oil still has more olefins than the Kentucky Hytort shale oils. This in part may be due to the fact the hydrogen pressure used in the IGT Hytort of the Colorado shale was lower than the hydrogen pressure used for the Eastern shales.

As expected, the hydrotreating of the Kentucky Hytort shale oils considerably reduces the mole percent of aromatics and olefins with a corresponding increase in the mole percent of alkanes.

CONCLUSIONS

It has been shown that computing the average molecular structure parameters from NMR data of shale oils can be useful in describing changes in the oils resulting from different retorting methods and source of the oil shale.

Eastern shale oils are more aromatic than the Western shale oil regardless of the retort method. It also has been observed that the IGT Hytort process increases the aromatic content and lowers the olefinic content of the Eastern shale oils, relative to the Fischer assay method.

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TABLE I ELEMENTAL ANALYSES OF SHALE OILS AND HYDROTREATED SHALE OILS

	Elemental Analysis, Wt%			
	Fischer Assay		IGT-Hytort	IGT-Hytort Hydrotreated
	A	B		
<u>Colorado Shale Oil</u>				
Carbon	85.08	84.30	84.57	
Hydrogen	11.44	11.42	11.40	
Sulfur	.73	.63	0.62	
Nitrogen	1.80	1.90	2.13	
Oxygen	1.31	1.50	0.98	
H/C Weight Ratio	0.135	0.136	0.135	
<u>Kentucky New Albany Shale Oil</u>				
Carbon	84.91	84.97	85.46	88.27
Hydrogen	9.83	10.08	9.42	11.70
Sulfur	1.02	1.61	1.52	.05
Nitrogen	1.52	1.56	2.12	.40
Oxygen	1.72	2.00	1.61	.12
H/C Weight Ratio	0.116	0.119	0.110	0.133
<u>Kentucky Sunbury</u>				
Carbon	84.36	84.59	85.45	87.30
Hydrogen	9.96	9.98	9.56	12.60
Sulfur	1.33	1.59	0.99	.06
Nitrogen	1.33	1.48	2.12	.17
Oxygen	2.12	2.36	1.22	.28
H/C Weight Ratio	0.118	0.118	0.112	0.144

TABLE II AVERAGE MOLECULAR STRUCTURE PARAMETERS AND MOLE PERCENT AROMATICS, OLEFINS, AND ALKANES FOR COLORADO SHALE OILS OBTAINED FROM THE FISCHER ASSAY AND IGT HYTORT PROCESSES

	Shale Oil Processes		
	Fischer Assay		IGT Hytort
	A	B	
Hydrogen Aromaticity	.054	.055	.070
Carbon Aromaticity*	.244	.244	.269
Mole Percent Aromatics**	26.5	26.1	28.1
Percent Mono-	24.9	24.3	25.3
Percent Di-	1.6	1.8	2.8
Fraction of Substituted & Bridged Carbons	.158	.154	.156
Fraction of Unsubstituted Carbons	.087	.090	.123
Number of Alkyl Substituents/Ring	3.3	3.2	2.8
Mole Percent Olefins	6.3	7.2	4.9
Mole Percent Alkanes	67.2	66.7	66.9
Fraction of n-alkanes	.35	.40	.51
Fraction of Branched Alkanes***	.65	.60	.49
CH ₂ /CH ₃ Ratio	2.1	2.3	2.2
Carbon Chain-Length	11.7	14.3	17.1
Total Atomic H/C Ratio	1.60	1.61	1.61
Aromatic H/C Ratio	.36	.37	.42
Alkane H/C Ratio	2.01	2.02	2.04

* Includes olefinic carbons

** Includes heteroaromatics

*** Includes cyclic alkanes and alkyl substituent carbons on aromatic rings

TABLE III AVERAGE MOLECULAR STRUCTURE PARAMETERS AND MOLE PERCENT AROMATICS, OLEFINS AND ALKANES FOR KENTUCKY NEW ALBANY SHALE OILS OBTAINED FROM THE FISCHER ASSAY, IGT HYTORT AND HYDROTREATMENT PROCESSES

	Fischer Assay		Shale Oil Processes	
	A	B	IGT Hytort	IGT Hytort Hydrotreated
Hydrogen Aromaticity	.102	.114	.171	.078
Carbon Aromaticity*	.362	.373	.468	.177
Mole Percent Aromatics**	46.4	46.9	60.0	32.9
Percent Mono-	41.1	42.5	51.4	30.0
Percent Di-	5.3	4.4	5.6	2.9
Fraction of Substituted & Bridged Carbons	.244	.212	.221	.055
Fraction of Unsubstituted Carbons	.225	.161	.141	.123
Number of Alkyl Substituents/Ring	3.0	2.8	2.3	2.7
Mole Percent Olefins	4.4	5.1	4.0	0.0
Mole Percent Alkanes	49.2	48.0	39.1	67.1
Fraction of n-alkanes	.29	.29	.27	.23
Fraction of branched alkanes***	.71	.71	.73	.77
CH ₂ /CH ₃ Ratio	1.04	.9	.8	1.1
Carbon Chain-Length	9.2	10.7	10.0	11.2
Total Atomic H/C Ratio	1.38	1.41	1.31	1.58
Aromatic H/C Ratio	.39	.43	.48	.69
Alkane H/C Ratio	1.94	2.00	2.05	1.77

* Includes olefinic carbons

** Includes heteroaromatics

*** Includes cyclic alkanes and alkyl substituent carbons on aromatic rings

TABLE IV AVERAGE MOLECULAR STRUCTURE PARAMETERS AND MOLE PERCENT AROMATICS, OLEFINS, AND ALKANES FOR KENTUCKY SUNBURY SHALE OILS OBTAINED FROM THE FISCHER ASSAY, IGT HYTORT AND HYDROTREATMENT PROCESSES

	Fischer Assay		Shale Oil Processes	
	A	B	IGT Hytort	IGT Hytort Hydrotreated
Hydrogen Aromaticity	.126	.119	.171	.048
Carbon Aromaticity*	.383	.382	.453	.184
Mole Percent Aromatics**	52.3	48.7	62.9	19.8
Percent Mono-	47.9	41.8	53.6	17.3
Percent Di-	4.5	6.9	9.4	2.5
Fraction of Substituted & Bridged Carbons	.205	.214	.225	.101
Fraction of Unsubstituted Carbons	.178	.168	.229	.084
Number of Alkyl Substituents/Ring	2.7	2.8	2.5	2.7
Mole Percent Olefins	6.6	6.0	3.1	0.0
Mole Percent Alkanes	41.1	45.3	33.9	80.2
Fraction of n-alkanes	.31	.31	.28	.22
Fraction of branched alkanes***	.69	.69	.72	.78
CH ₂ /CH ₃ Ratio	.6	.7	.3	1.3
Carbon Chain-Length	10.0	9.7	10.4	8.7
Total Atomic H/C Ratio	1.41	1.41	1.33	1.72
Aromatic H/C Ratio	.46	.44	.50	.45
Alkane H/C Ratio	1.99	2.00	2.02	2.00

* Includes olefinic carbons

** Includes heteroaromatics

*** Includes cyclic alkanes and alkyl substituent carbons on aromatic rings

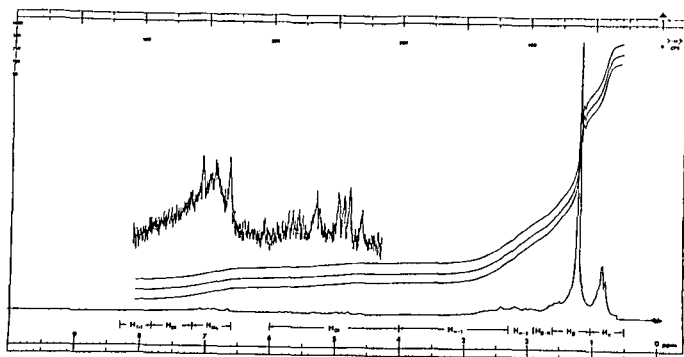
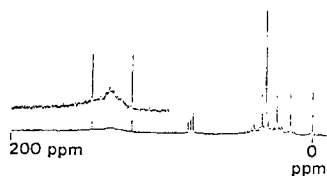


Figure 1 ^1H NMR SPECTRUM OF THE COLORADO SHALE OIL OBTAINED FROM THE FISCHER ASSAY METHOD

Carbon-13 NMR

Colorado Shale Oil
Fischer Assay



IGT Hytort Process

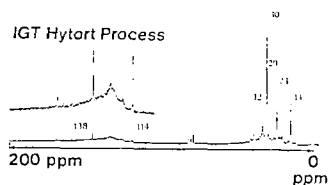
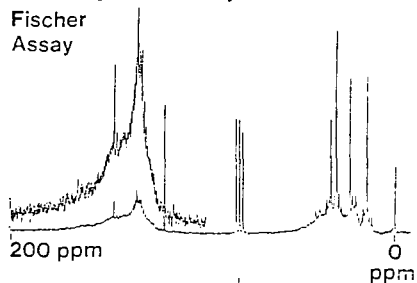


Figure 2 ^{13}C NMR SPECTRA OF THE COLORADO SHALE OILS OBTAINED FROM THE FISCHER ASSAY AND IGT HYTORT PROCESSES

Carbon-13 NMR

Kentucky New Albany Shale Oil
Fischer
Assay



IGT Hytort Process

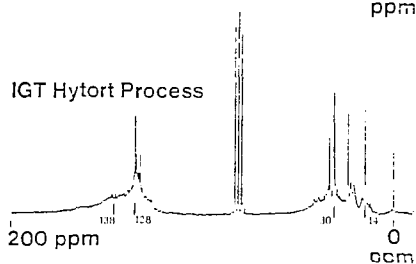


Figure 3 ^{13}C NMR SPECTRA OF THE KENTUCKY NEW ALBANY SHALE OILS OBTAINED FROM THE FISCHER ASSAY AND IGT HYTORT PROCESSES

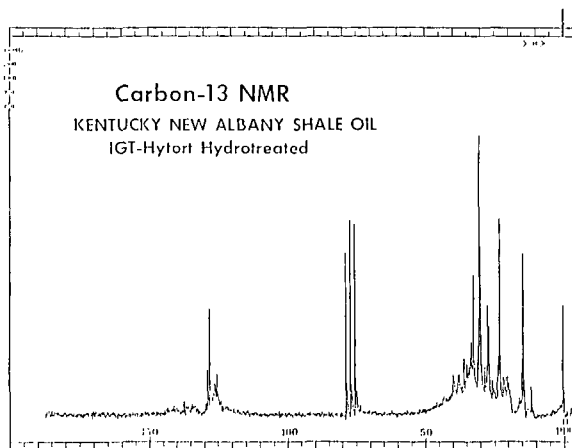


Figure 4 ^{13}C NMR SPECTRUM OF THE HYDROTREATED KENTUCKY NEW ALBANY SHALE OIL OBTAINED FROM THE IGT HYTORT PROCESS